



Coleman, Simon J. and Roy, Sudipta (2018) Design of an ultrasonic tank reactor for copper deposition at electrodes separated by a narrow gap. Ultrasonics Sonochemistry, 42. pp. 445-451. ISSN 1350-4177 , <http://dx.doi.org/10.1016/j.ultsonch.2017.11.038>

This version is available at <https://strathprints.strath.ac.uk/62489/>

Strathprints is designed to allow users to access the research output of the University of Strathclyde. Unless otherwise explicitly stated on the manuscript, Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Please check the manuscript for details of any other licences that may have been applied. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (<https://strathprints.strath.ac.uk/>) and the content of this paper for research or private study, educational, or not-for-profit purposes without prior permission or charge.

Any correspondence concerning this service should be sent to the Strathprints administrator: strathprints@strath.ac.uk



Design of an ultrasonic tank reactor for copper deposition at electrodes separated by a narrow gap

Simon J. Coleman*, Sudipta Roy

Department of Chemical and Process Engineering, University of Strathclyde, James Weir Building, 75 Montrose Street, Glasgow G1 1XJ, UK

ARTICLE INFO

Keywords:

Copper
Electrodeposition
Ultrasonic
Reactor design
Mass
Transfer
Maskless

ABSTRACT

This work describes the design and testing of an ultrasonic reactor suitable for processes which require agitation within a narrow gap in a tank geometry. A maskless microfabrication process was used to validate the ultrasonic reactor design. This mask-less electrodeposition method requires the inter-electrode distance between the anode tool and the cathode substrate to be maintained at 300 μm , and sufficient stirring of the electrolyte by ultrasound agitation. A design was proposed allowing 74 mm \times 105 mm size substrates to be mounted into an electrode holder and loaded into an 18 L ultrasonic reactor. Experiments were carried out to test the uniformity of the mass transfer within the narrow electrode gap at different locations on the substrate, and to validate the feasibility of a mask-less metal plating technique by depositing features of μm -scale. When increasing ultrasonic powers from 30 to 60 W L^{-1} , increasing agitation was observed at the centre of the substrate, but not at its edges. A Sherwood number correlation showed developing turbulence within the narrow gap, even in the centre of the plate. Micron scale features were plated onto A7 substrates, but the deposited features were 2.5 times the original width. The work showed that sonic streaming can produce sufficient agitation in long sub millimetre channels which can be employed to overcome mass transfer limitations.

1. Introduction

Microfabrication is used to construct functional patterns onto surfaces as part of the manufacturing process for a variety of devices, including micro-fluidics, MEMS, micro-optic and micro-electronic systems [1,2]. These devices commonly require through-mask metal deposition [1–4]; the mask typically being fabricated using photolithography [5]. Despite its popularity, photolithography has many disadvantages: (1) it is a complex multi-step process, (2) the process uses hazardous chemicals, (3) which produces a large amount of waste, and (4) requires specialised expensive infrastructure.

A variety of techniques have been proposed to reduce the use of photolithography [6–11]. This includes a variety of additive electrochemical techniques, such as localised electrodeposition [6], electrochemical printing [7], Inkjet techniques [8], and direct writing [9,10]. One such technology is Enface [11], in which, instead of applying a mask to the substrate surface, photolithography is carried out on a tool. The patterned tool is then placed in close proximity ($< 500 \mu\text{m}$) to the substrate. A current is passed between the two electrodes, thereby selectively etching or plating the desired metal pattern onto the unmasked substrate. Since the tool can be used repeatedly to pattern many substrates, this technique can significantly reduce the use of

photolithography.

Previous experimental attempts of this technique have focused on transferring metallic patterns on small-scale substrates of 10 mm diameter [12–15]. Modelling the process suggested an inter-electrode gap of 300 μm was required to transfer metallic features between 5 and 100 μm [16]. The results also showed that forced convection within this narrow inter-electrode gap was necessary to ensure sufficient delivery of fresh solution and removal of by-products. Owing to the importance of agitation in this process, a parallel plate electrochemical flow cell was used to provide forced convection in experiments, which was adapted from an earlier work where electrodes were not in close proximity [17]. That flow system cannot be deployed for larger electrodes due to high pressure drops in channel flow through a narrow gap. Further experimental results showed that natural convection conditions also did not provide sufficient agitation within the inter-electrode gap [14,18]. These natural and forced convection results proved that in order to use the same technique for patterning larger substrates, an appropriate agitation method within the electrode gap was necessary.

Ultrasonic (US) agitation has been shown to improve stirring in electrochemical systems [19–21] due to cavitation phenomena [22–24]. Therefore, the authors of this paper carried out experiments to

* Corresponding author.

E-mail address: simon.coleman.sjc@gmail.com (S.J. Coleman).

determine if *US* agitation could be used to provide stirring for metallisation using Enface technique [15,25–29]. An initial assessment using an *US* probe placed within a 500 mL ‘beaker-type’ system was shown to improve mass transfer by ten-fold during copper deposition within an electrode gap of 1500 μm [25]. This suggested that *US* agitation could be a suitable agitation technique for the Enface method. Further copper deposition experiments using 10 mm diameter substrates showed that fluid agitation effectively removed bubbles and etched material from the inter-electrode gap [15,26,27] thereby improving deposit properties [15].

However, it has also been found that employment of an *US* probe can cause potential distortions within an electrochemical cell [25,30] and not useful for scale up purposes. Therefore for larger scale applications, an *US* bath may be a more suitable apparatus. Additionally, more uniform agitation is achieved within the tank of an *US* bath compared to employing an *US* probe [31], which could ensure similar material transport across a large substrate. However, the intensity of the *US* power is generally lower in bath systems than in probe systems [32]. Currently, only limited information is available for *US* applications using a bath [33]. Therefore it is unclear if such an apparatus can be used for providing agitation within a narrow gap.

This work reports the design and testing procedure using a large-scale *US* tank which could provide adequate fluid agitation within a narrow inter-electrode gap. This design would be suitable for reaction systems where mass transfer limitations occurred due to the proximity of reaction surfaces. The design and testing has focused on copper electrodeposition and micro-fabrication by using 74 mm \times 105 mm substrates. Copper plating is chosen because it is well known that Cu reduction is characterised by fast kinetics and slow material transport. This reactor design should also be suitable for reaction systems where mass transfer limitations occurs in a narrow gap. The main aims of this work were to: (i) assess mass transfer within a narrow gap between two substrates of 74 mm \times 105 mm, which correspond to an A7 size, placed in an 18 L tank; (ii) testing the uniformity of the mass transfer at different locations on the substrate and developing a mass transfer correlation; (iii) and perform mask-less metal plating at the μm -scale as a verification of its usefulness applicability of *US* agitation to.

2. Reactor design

2.1. Electrode holders

At first a design was proposed which would allow A7 size substrates to be mounted into the electrode holder and loaded into the reactor. The design had to consider that the plates had to be contacted to the power supply (but sealed against any electrolyte ingress to avoid shorting), and be dismantled after deposition, washed and extracted from the holder without touching the deposit or the substrate surface.

Fig. 1 shows the electrode holders used in the deposition experiments. The holders were fabricated from two PVC blocks and were designed to hold two A7 size electrode plates. The electrodes were made from high conductivity oxygen-free copper plates (*Advent*). The holders were screwed together with plastic bolts so the plates face each other with an electrode gap between them. The electrical connection was made from the back of the plate. When the holders were screwed together, the plate was pressed tightly against a copper block at the back of the holder. A copper rod was screwed into the top of the block to which electrical contacts were connected. Electrical insulation covered the area of the copper rod that was submerged in the electrolyte to prevent any electrical contact with the electrolyte solution. A Perspex rod was also screwed into the holder for extra support. These rods were then screwed into a support block above so the holders could be suspended in the solution, as shown in Fig. 2.

In order to ensure that the inter-electrode gap was accurate, spacers made from PTFE sheet were placed in the corners and middle of the plate. For the mass transfer experiments, a gap of 1.5 mm was used.

This allowed the authors to compare data obtained for the A7 substrates with those obtained for smaller ones [25]. An electrode gap of 0.3 mm, or 300 μm , was used for the micro-scale pattern deposition. The accuracy and variation in the inter-electrode gap was measured by applying silicone sealant at various locations on the copper plate. The spacers were placed into position and the holders were screwed together. The silicone was then left to dry, after which the holders were unscrewed and taken apart. An optical microscope was then used to measure the thickness of the dried silicone sealant at different locations on the plate. These measurements showed that there was a variation of $\pm 40 \mu\text{m}$ across the plate. This variation arose due to the natural curvature of the metal substrate and therefore could not be eliminated.

2.2. Electrodes and tools

Mass transfer experiments were carried out in the *US* tank by using a tool such as shown in Fig. 3(a) to measure the limiting current at two different locations. This tool was a 1 mm thick Perspex sheet with 10 mm \times 10 mm square holes, into which 10 mm \times 10 mm polished copper squares could be slotted. This tool was placed into the electrode holder with a copper foil placed behind it which allowed for electrical connection from the back. The slotted copper squares then served as anodes for experimentation. An A7 copper plate, placed in the opposite holder, served as the cathode. Either of the squares, A or B, could be connected up individually to the electrical connection. This made it possible to measure the limiting current at the corner and near in the middle of the plate separately. These locations were important, since one site is more accessible for ionic species; a comparison of mass transfer conditions would allow one to estimate the differences in material transport at the two positions. In particular, A is located at the centre, just above the spacer which could impede mass transfer.

Micron scale features were electrodeposited using a specialised anode (which is referred to as tool) and cathode. Both the anode and cathode were made from high conductivity oxygen-free copper plates (*Advent*), cut into A7 size rectangles. The substrates were washed thoroughly with diluted Decon 90 solution and polished manually with #1200, #2400 and #4000 grit SiC paper. They were then rinsed with deionized water and dried thoroughly using a nitrogen gun. The anode was then masked by E9230 dry resist with μm -scale linear features (210 μm width lines of exposed copper surface, with 1040 μm width lines of resist between each exposed copper line), such as that shown in Fig. 4(a). Linear features were chosen to evaluate if *US* agitation: (1) caused photoresist delamination during electrodeposition, and (2) if there was significant differences in replication of pattern at different locations of the tool. The protocol for the fabrication of this tool is described elsewhere [34].

2.3. The tank

US agitation was provided by a *Hilsonic US* tank with a capacity of 18 L, which is the smallest size used in industrial plating applications. Since the system was to be used for electrodeposition of copper from an acid bath containing chloride ions, a hard enamel coating was applied to the walls to prevent the steel walls coming into electrical contact with the electrolyte solution. Fig. 2 shows the location of the transducers on the walls of the tank, with 5 transducers on each side-wall and 4 on the bottom. The transducers operated at a frequency of $30 \pm 2 \text{ kHz}$ and three different powers, 30, 40 and 60 W L^{-1} , were used in the experiments. Although these powers would normally produce sufficient agitation within the tank, the stirring within a narrow gap is severely restricted due to the limited penetration of flow of ultrasonic streaming, which needs investigation. In each experiment, the electrode holder was immersed into the *US* tank and placed into the position so that the locations of the transducers are situated side-on to the electrodes. The electrodes had to be positioned at distances further than 30 mm from the walls of the tank, in order to obtain an even *US* agitation. The *US*

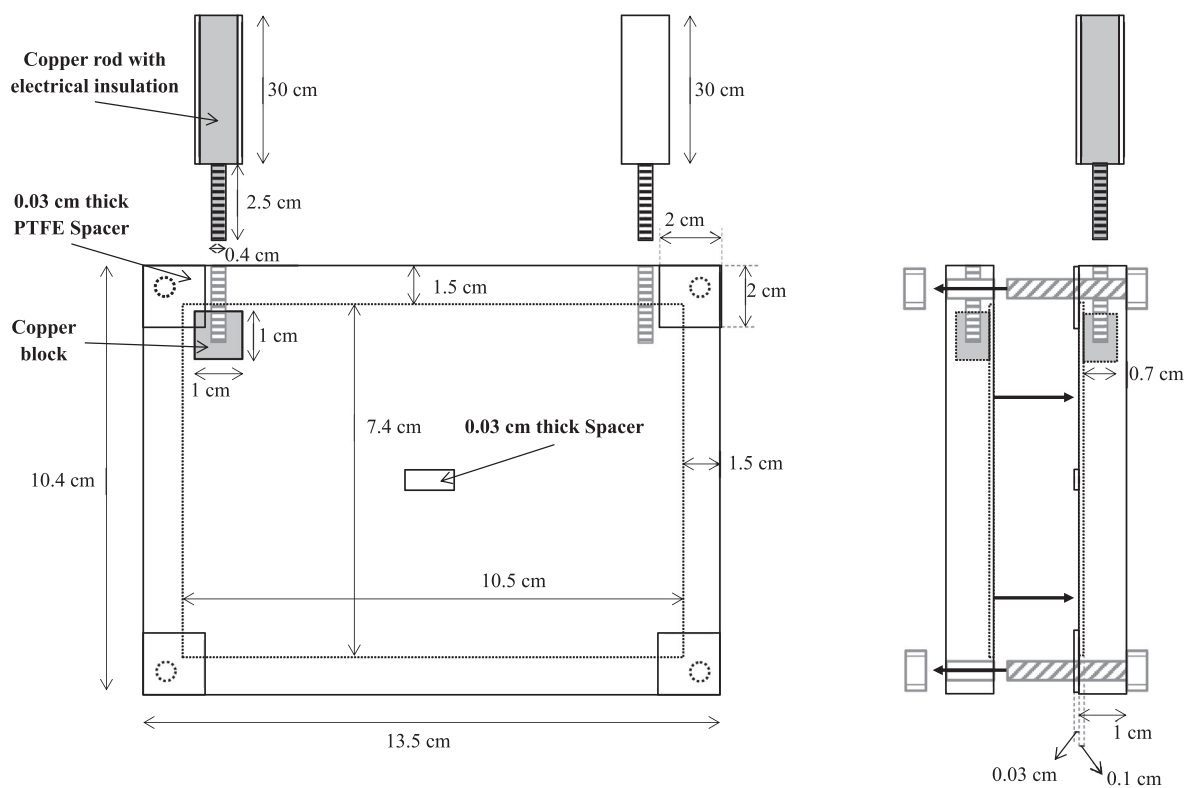


Fig. 1. Design of Electrode Holder for A7 size electrode plates.

power was calibrated using a standard power calibration procedure [35].

3. Electrodeposition experiments

3.1. Mass transfer experiments

Mass transfer within the narrow gap was examined using limiting current method to determine diffusion layer thicknesses. The limiting

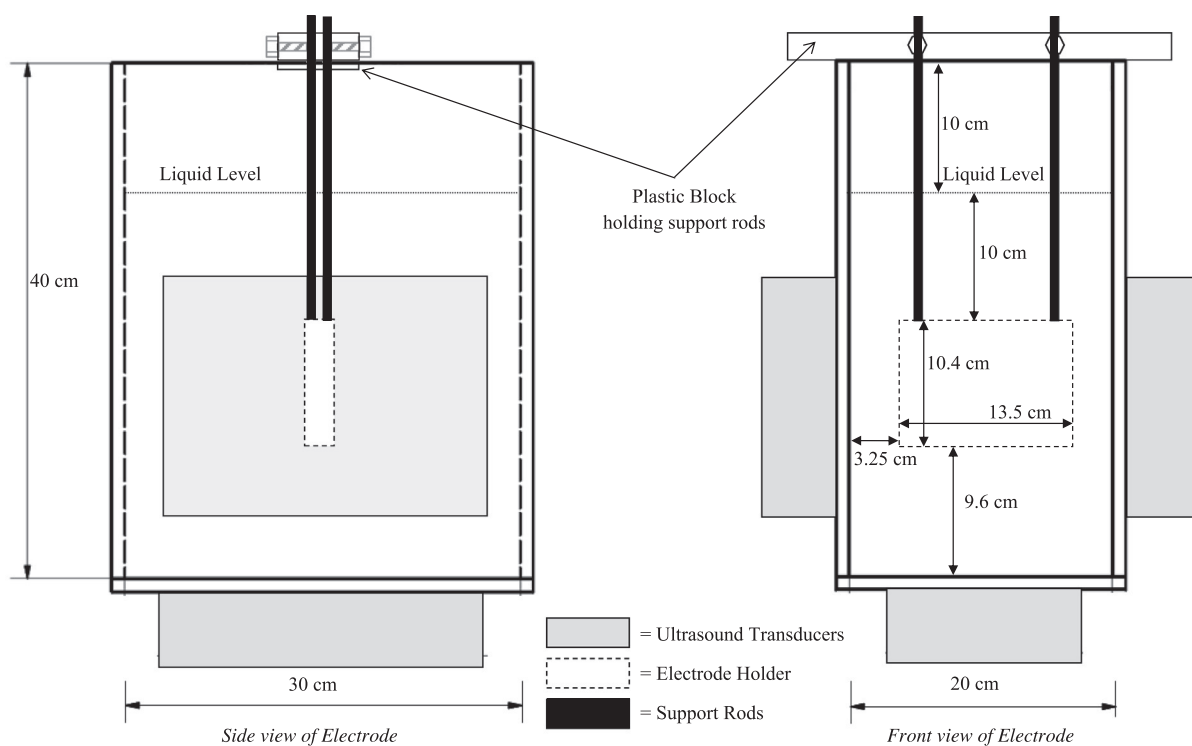


Fig. 2. Ultrasonic Tank showing position of transducers and placement of Electrode Holder.

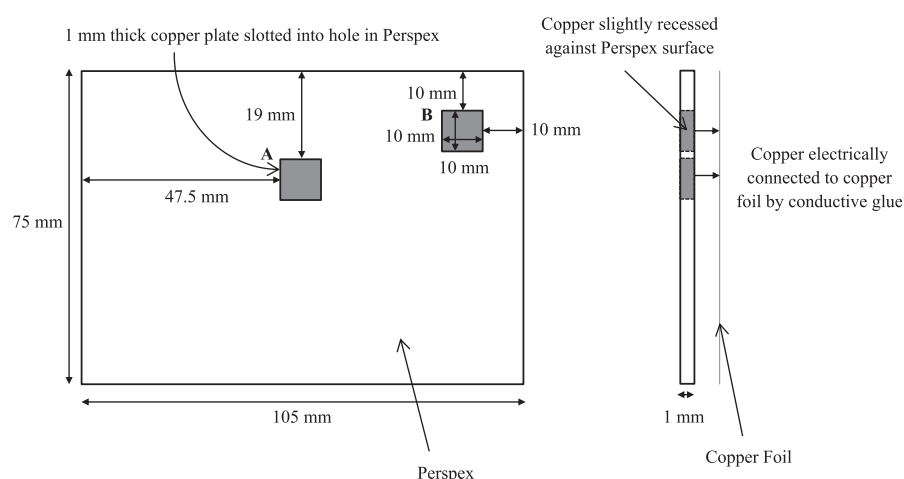


Fig. 3. Tool used for limiting current experiments in the US tank.

current measurements were carried out galvanostatically using a two electrode system, although limiting current experiments would normally require the electrode potentials to be measured. However, it is well known that potential at large electrodes, such as the ones used in these experiments, aren't suitable for measurement of electrode potentials [25]. In addition, using reference electrodes for such measurements in narrow channel can corrupt potential data [25]. In these experiments, therefore, current densities between 10 and 140 mA cm⁻² were applied for 30 s to allow the system to stabilise, after which the cell potential was measured using a multimeter. A *Thurlby Thander* power supply was used to apply the current. Experiments were carried out at either 30, 40 or 60 WL⁻¹ under continuous wave conditions. The electrolyte solution used for the mass transfer experiments was 0.1 M CuSO₄ with 0.1 M H₂SO₄. Each limiting current measurement was repeated 3 times to check for reproducibility.

3.2. Validation by electrodeposition μ -scale features

For each pattern deposition experiment, the A7 size copper substrates were washed with diluted Decon 90 solution and polished with #1200, #2400 and #4000 grit SiC paper before drying thoroughly with a nitrogen gun. The electrodes were then placed in their holders and assembled. A multimeter was used to check the electrical connection from the rod to the plate before positioning the spacers and screwing the holders together. The Perspex support rods and support bar were attached and then the holders were submerged into the solution in the US tank, ensuring that no air was trapped within the electrode gap. An acid free electrolyte containing 0.1 M CuSO₄ was used in these experiments. Earlier studies [12,13,16] have shown that pattern

replication is enabled if the conductivity of the solution is low.

In each experiment, a *Thurlby Thander* power supply was used to apply a direct current (DC) and the cell potential was measured with a multimeter during plating. All three generators were used to agitate the fluid using US powers of 30, 40 or 60 WL⁻¹. A current density of 20 mA cm⁻² was applied for a plating time of 677 s to obtain a deposit thickness of 5 μ m. The US generators were switched off after plating and the electrode holder was removed from the US tank and immediately placed into a deionized water rinse bath. The electrode holder was then dismantled and the electrodes were removed. The extracted substrate was then dried thoroughly with a nitrogen gun.

Profilometry of the deposited features was carried out to measure the feature width and thickness as well as to measure the deposit roughness (R_a). Profiles of each deposit were measured using a *Tencor P-1 Long Scan Profilometer* across the middle of the deposit pattern feature. The thickness of the deposit was taken as the average height of the profile in the centre of the deposit over a 7 mm region. The value of R_a for each deposit was calculated over a 3000 μ m region, and was measured in 3 locations of each profile; near the left side, near the right side and in the centre of the profile. Each deposition experiment was repeated 3 times and the average R_a of these 3 repeats was taken as the average deposit roughness. Corrective measures to adjust for the intrinsic curvature within the plate using a standard technique was taken and is described elsewhere [36].

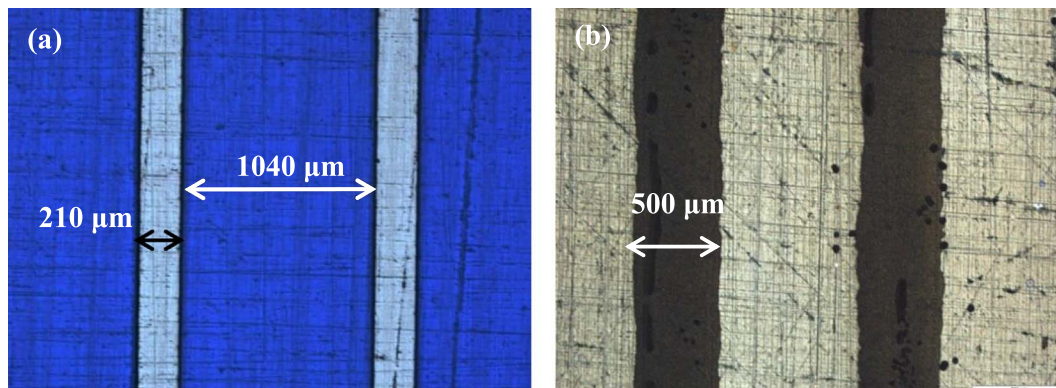


Fig. 4. Optical microscope images with magnification $\times 5$. (a) Dry photoresist pattern on the anode (b) Deposited features via maskless plating at 20 mA cm⁻² under DC conditions at 40 WL⁻¹ US power.

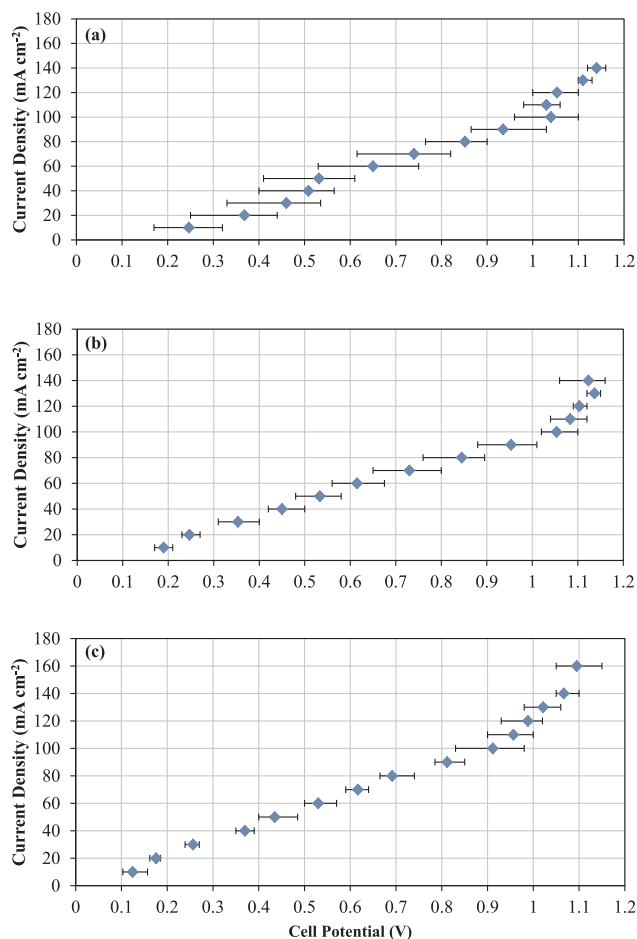


Fig. 5. Limiting current experiments in ultrasonic tank with 0.1 M CuSO_4 + 0.1 M H_2SO_4 electrolyte, using a tool with slot A copper anode. Inter-electrode gap is 1.5 mm and ultrasound operating at ultrasonic powers of (a) 30 W L^{-1} , (b) 40 W L^{-1} and (c) 60 W L^{-1} .

4. Results and discussion

4.1. Mass transfer experiments

Cell potential vs. cathodic current density for the limiting current experiments are shown in Figs. 5 and 6. As mentioned, the cell potential was measured as opposed to the electrode potential, due to the difficulty of the inclusion of a reference electrode in this narrow geometry. The error bars denote the range of current fluctuations observed during the experiment and is caused due to cavitation [20,37]. The limiting current, at both locations, is difficult to discern easily due to the slope of current vs. potential data. In fact, at potentials higher than 0.9 V, the currents show a shift towards lower potentials (which is clearly visible in Fig. 6a), this can occur due to deposit roughening when the i_{Lim} is reached or exceeded [38].

The value of limiting current was determined from asymptotes at low and high cell potentials as shown in Fig. 6c. This approach has been used by a variety of researchers when a clear limiting current is not observed [39,40]. The values of i_{Lim} at the location B was determined to be 70, 80 and 90 mA cm^{-2} at US powers of 30, 40 and 60 W L^{-1} respectively, illustrating that increased agitation occurs with increasing power. In contrast, the value of limiting current is calculated to be $\sim 80 \text{ mA cm}^{-2}$ for all three US powers at location A (see Fig. 6). This suggests that US power within the range investigated here can provide increasing agitation at the centre, but does not affect the mass transfer at the edges.

The diffusion boundary layer thickness (δ) for the limiting currents

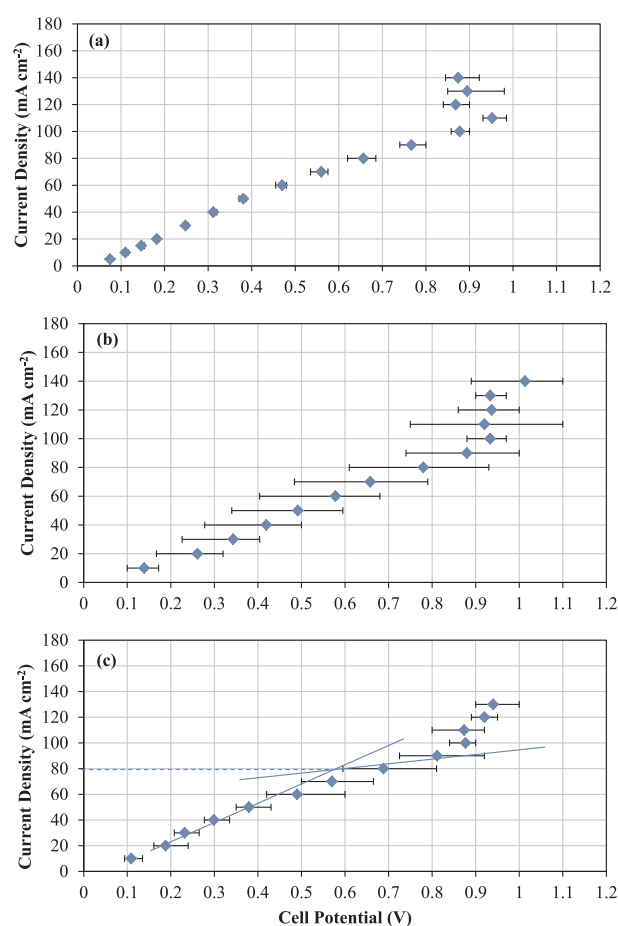


Fig. 6. Limiting current experiments in ultrasonic tank with 0.1 M CuSO_4 + 0.1 M H_2SO_4 electrolyte, using a tool with slot B copper anode. Inter-electrode gap is 1.5 mm and ultrasound operating at ultrasonic powers of (a) 30 W L^{-1} , (b) 40 W L^{-1} and (c) 60 W L^{-1} .

is calculated using the relationship in Eq. (1).

$$|i_{\text{Lim}}| = \frac{nFDC_b}{\delta} \quad (1)$$

The value of δ was calculated to range between 15 and $19 \mu\text{m}$ at A (presented in Table 1), whereas δ was a similar value of $17 \mu\text{m}$ for all US powers at B. Similar thicknesses of the mass transfer boundary layer were also found at smaller electrodes [25] using an US probe with a power of 48 W L^{-1} . Therefore, one can conclude that the agitation conditions within a narrow gap in an US tank and large electrodes for powers between 30 and 60 W L^{-1} are similar to those induced by an US probe operating at powers between 24 and 77 W L^{-1} .

In order to predict mass transfer across from location A, where agitation is likely to be limited, a mass transfer condition is required. Therefore, a dimensionless analysis was carried out using literature values of diffusion coefficient (D) and kinematic viscosity (ν) of values of $7.066 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $1.004 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, respectively [41].

Table 1

Diffusion layer thickness at position A, calculated fluid velocity and dimensionless numbers at various ultrasound powers in the 18 L ultrasonic tank.

Power (W L^{-1})	Diffusion layer thickness, δ (μm)	Sh	Velocity, U (cm s^{-1})	Re
30	19	513	32	839
40	17	587	41	1068
60	15	660	59	1525

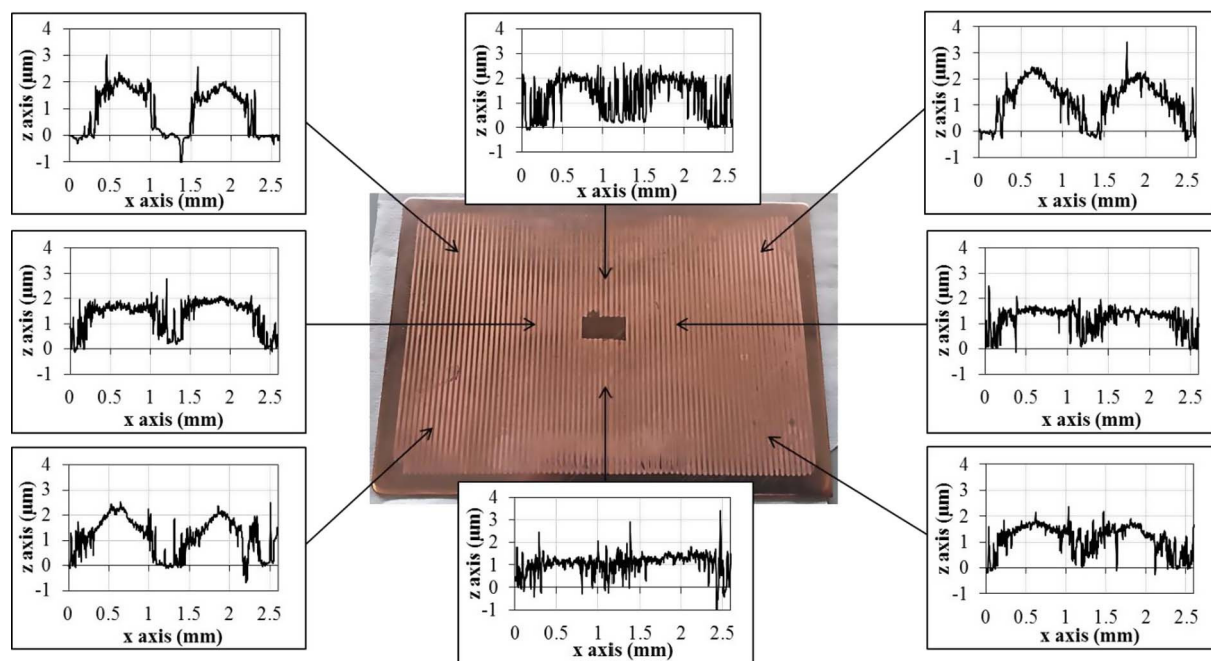


Fig. 7. A7 size copper cathode substrate after plating in ultrasonic tank using dry resist tool with linear pattern features; plated with DC current density of 20 mA cm^{-2} , with all 3 generators using a US power of 40 W L^{-1} ; Profiles taken across two features.

The hydraulic diameter (d_H) was 0.2609 cm , calculated using the method previously described [25] and an electrode gap of 1.5 mm was used. However, a problem arises in describing velocities within the gap. To the best of the author's knowledge there are no studies where the fluid flow within a narrow gap under *US* agitation has been modelled. Although investigations have been carried out to measure pressure changes [33] and cavitation activity [31,42] at different locations, there was no measurement of flow velocity.

In absence of such data, a velocity description developed by Eklund [43], for free flow at electrodes with varying distances from a *US* probe, that was used by the authors previously [25] was employed here. It is important to note that the fluid velocities provided by Eklund's relationship [43] are different from the conditions here, mainly because Eklund's geometry was for a 'free electrode' and this system is investigating a narrow channel flow. In addition, the current experiments use three generators rather than a point where a probe is located. However using an approximate value of velocity allows one to develop approximate mass transfer correlations which can elucidate the agitation conditions within the narrow gap.

The different fluid velocities, using this approach, and the corresponding Sherwood number and Reynolds number for each *US* power is shown in Table 1. The Sherwood-Schmidt-Reynolds number correlation arising from these calculations for the central location at the electrode is also shown in Eq. (2).

$$Sh = 2.77 \left(ReSc \frac{d_e}{L} \right)^{0.41} \quad (2)$$

The mass transfer correlation shows that developing turbulent conditions prevail at the central location of the large substrate. Previous work on a small-scale system showed that fully developed turbulence occurred within such a narrow gap when a 1 cm diameter electrode was used [25]. Although, turbulences occur due to the interaction between the momentum boundary layers at the entrances of the channel, differences in flow velocity arise due to length of the channel. This behaviour is similar to earlier copper deposition using long electrodes (75 mm) where developing turbulence was observed [44].

4.2. Validation by electrodeposition of μm -scale features

The dry resist tool shown in Fig. 4a was used to test the replication of linear μm -scale features on the substrate by electrodeposition. Based on the mask design, the total area exposed to the electrolyte (i.e. area where electrochemical dissolution took place) was 10.6 cm^2 . A current of 211 mA was applied for each experiment to achieve 20 mA cm^{-2} based on this anode area. All mask-less deposition experiments were carried out using an *US* power of 40 W L^{-1} and a plating time of 677 s , which would allow a nominal deposit thickness of $5.0 \mu\text{m}$ if the feature width were exactly replicated.

A detail from the optical microscope image of the anode features and cathode deposit is shown in Fig. 4a and b. The width of linear feature at the anode tool is $210 \mu\text{m}$, and each exposed strip is separated by $1040 \mu\text{m}$. The width of the deposit at the cathode, however, was found to be typically $540 \pm 120 \mu\text{m}$, which is 2.5 times larger than the anode feature. This increase in feature size is due to the effect of current spreading. Earlier studies of mask-less deposition of copper using En-face technology and the same electrolyte have shown that increase in feature size can be limited to less than 20% [12,13]. The larger current spread in the current experiments could be due to the processes accompanying cavitation.

A full A7 copper plate with μm -scale features plated at a current density of 20 mA/cm^2 is presented in Fig. 7. The figure shows that copper features have been plated over the entire substrate. However, profiles of the deposit thickness and roughness at different locations show considerable differences. The data reveals that features at the bottom of the plate, i.e. those closest to the *US* transducers have the poorest replication. The average roughness, R_a , of the features was 0.11 ± 0.06 across the entire substrate, independent of location. The average thickness of the μm -scale deposits was found to be close to $1.9 \mu\text{m}$, as would be expected from the feature width and a current efficiency close to 100% [45].

In order to probe more deeply why poor replication occurs towards the bottom of the substrate, the adherence of the photoresist to the anode tool was also tested in a separate set of experiments. In these cases, anode tools with resist features of $145 \mu\text{m}$, $320 \mu\text{m}$ and $1000 \mu\text{m}$ (i.e. 1 mm) were fabricated and placed in the *US* tank and subjected to

US agitation at 40 WL^{-1} . After approximately 10 mins the $145 \mu\text{m}$ lines of resist were found to completely de-adhere from the tool. Some damage was also observed for the $320 \mu\text{m}$ lines. The tool with line widths of $1000 \mu\text{m}$ was found to be undamaged; and it was found to remain intact for over 50 mins, which would be the time required to deposit one substrate. These experiments showed that poor replication was due to the damage to the anode tool. Since many micro-fabricated parts require the transfer of features of $100 \mu\text{m}$, it is important that US power should be optimised such that photolithographed tools remain unaffected. Possibly, lower US power, where resist delamination does not occur, could be an alternative. This has been examined in a separate study by our group, Serra et al., [29]. Interestingly, the work by the authors in the present paper (Coleman and Roy) has shown that it is possible to use ultrasonic agitation within the narrow gap between two plates using an ultrasonic tank reactor, even when the plates are size A7. This therefore suggests that an ultrasonic tank can be used in applications that require fluid agitation within restricted geometries with a channel length of 10 cm in magnitude.

5. Conclusion

This paper reports on the design and verification of an US tank which is capable of providing agitation of A7 scale substrates for use in micron scale pattern transfer using a mask-less electrochemical method. The design for electrode holders which allow the anode and cathode to be placed a close proximity, i.e. within $500 \mu\text{m}$ is discussed. The ability to agitate the fluid using US agitation within the narrow gap between the two electrodes was tested using the limiting current technique, at two different locations of the cathode. When increasing US powers from 30 to 60 WL^{-1} increasing agitation was observed at the centre of the substrate, but did not affect the mass transfer at its edges. A predictive Sherwood number correlation was developed for the agitation within the narrow gap. Mass transfer conditions within a narrow gap in an US tank and large electrodes were found to be similar to those induced by an US probe operating at similar US powers. Micron scale features were plated using this apparatus on A7 substrates. It was found that deposited features were almost 2.5 times the original width; and some of this was due to the damage to the resist due to ultrasound. Our findings show that sonic streaming can produce sufficient agitation in long sub millimetre channels which can be employed to overcome mass transfer limitations.

Acknowledgements

This work was done at Newcastle University. Simon Coleman acknowledges the studentship support by EPSRC, UK grant EP/J500288/1. The work was supported by EU 'MESMOPROC' Grant 303550. The Mechanical Workshop of CEAM (Newcastle University) is acknowledged for the fabrication and machining of the electrode holders.

References

- [1] M.J. Madou, *Fundamentals of Microfabrication and Nanotechnology (Volume II): Manufacturing Techniques for Microfabrication and Nanotechnology*, CRC Press, Boca Raton, 2012.
- [2] S. Franssila, *Introduction to Microfabrication*, 2nd ed., John Wiley & Sons, West Sussex, 2010.
- [3] M. Datta, D. Landolt, *Fundamental aspects and applications of electrochemical microfabrication*, *Electrochimica acta* 45 (15) (2000) 2535–2558.
- [4] K. Kondo, et al., *Copper Electrodeposition for Nanofabrication of Electronics Devices*, Springer, 2014.
- [5] L.T. Romankiw, E. Sullivan, *Plating Techniques Handbook of Microlithography, Micromachining and Microfabrication*, SPIE Press, Bellingham WA, 1997.
- [6] J.D. Madden, I.W. Hunter, *Three-dimensional microfabrication by localized electrochemical deposition*, *J. Microelectromech. Syst.* 5 (1) (1996) 24–32.
- [7] J.D. Whitaker, J.B. Nelson, D.T. Schwartz, *Electrochemical printing: software reconfigurable electrochemical microfabrication*, *J. Micromech. Microeng.* 15 (8) (2005) 1498.

- [8] A. Doraiswamy, et al., *Inkjet printing of bioadhesives*, *J. Biomed. Mater. Res. B Appl. Biomater.* 89 (1) (2009) 28–35.
- [9] S.R. Samarasinghe, et al., *Printing gold nanoparticles with an electrohydrodynamic direct-write device*, *Gold Bull.* 39 (2) (2006) 48–53.
- [10] J. Hu, M.-F. Yu, *Meniscus-confined three-dimensional electrodeposition for direct writing of wire bonds*, *Science* 329 (5989) (2010) 313–316.
- [11] S. Roy, *Fabrication of micro- and nano-structured materials using mask-less processes*, *J. Phys. D Appl. Phys.* 40 (22) (2007) R413.
- [12] I. Schönenberger, S. Roy, *Microscale pattern transfer without photolithography of substrates*, *Electrochimica acta* 51 (5) (2005) 809–819.
- [13] Q.-B. Wu, T.A. Green, S. Roy, *Electrodeposition of microstructures using a patterned anode*, *Electrochem. Commun.* 13 (11) (2011) 1229–1232.
- [14] T. Widayatno, S. Roy, *Nickel electrodeposition using EnFACE*, *J. Appl. Electrochem.* 44 (7) (2014) 807–820.
- [15] S. Coleman, S. Roy, *Electrodeposition of copper patterns using Enface technique under ultrasonic agitation*, *J. Appl. Electrochem.* 45 (8) (2015) 1–10.
- [16] S. Nouraei, S. Roy, *Electrochemical process for micropattern transfer without photolithography: a modeling analysis*, *J. Electrochem. Soc.* 155 (2) (2008) D97–D103.
- [17] S. Roy, Y. Gupta, T.A. Green, *Flow cell design for metal deposition at recessed circular electrodes and wafers*, *Chemical engineering science* 56 (17) (2001) 5025–5035.
- [18] T. Widayatno, *Micropattern Transfer without Photolithography of Substrate: Ni Electrodeposition using Enface Technology*, Newcastle University, 2013.
- [19] D.J. Walton, et al., *Sonovoltammetry at platinum electrodes: surface phenomena and mass transport processes*, *J. Appl. Electrochem.* 25 (12) (1995) 1083–1090.
- [20] R.G. Compton, et al., *Voltammetry in the presence of ultrasound: mass transport effects*, *J. Appl. Electrochem.* 26 (8) (1996) 775–784.
- [21] B. Pollet, *Power Ultrasound in Electrochemistry: From Versatile Laboratory Tool to Engineering Solution*, John Wiley & Sons, 2012.
- [22] T.J. Mason, J.P. Lorimer, *Applied Sonochemistry: The Uses of Power Ultrasound in Chemistry and Processing*, Wiley, 2002 pp. 1–48.
- [23] R. Ramachandran, R. Saraswathi, *Sono-electrochemical studies on mass transport in some standard redox systems*, *Russ. J. Electrochem.* 47 (1) (2011) 15–25.
- [24] E. Yeager, F. Hovorka, *Ultrasonic waves and electrochemistry. I. A survey of the electrochemical applications of ultrasonic waves*, *J. Acoustical Soc. Am.* 25 (3) (1953) 443–455.
- [25] S. Coleman, S. Roy, *Effect of ultrasound on mass transfer during electrodeposition for electrodes separated by a narrow gap*, *Chem. Eng. Sci.* 113 (2014) 35–44.
- [26] S. Coleman, S. Roy, *Combined pulsing currents and agitation for electrodeposition*, *Transactions of the IMF* 92 (6) (2014) 316–320.
- [27] S.J. Coleman, S. Roy, *Electrodeposition of Copper Patterns Using EnFACE Technique under Ultrasonic Agitation*, *Chem. Eng. Trans.* 41 (2014) 37–42.
- [28] S.J. Coleman, *Scale-up of Enface Electrochemical Reactor Systems (PhD Thesis)*, Newcastle University, 2015.
- [29] A. Serra, et al., *Sono-electrodeposition transfer of micro-scale copper patterns on to A7 substrates using a mask-less method*, *Electrochimica acta* 207 (2016) 207–217.
- [30] F. Marken, R.G. Compton, *Electrochemistry in the presence of ultrasound: the need for bipotentiostatic control in sonovoltammetric experiments*, *Ultrason. Sonochem.* 3 (2) (1996) S131–S134.
- [31] L. Csoka, S.N. Katekhaye, P.R. Gogate, *Comparison of cavitation activity in different configurations of sonochemical reactors using model reaction supported with theoretical simulations*, *Chem. Eng. J.* 178 (2011) 384–390.
- [32] R.G. Compton, J.C. Eklund, F. Marken, *Sono-electrochemical processes: a review*, *Electroanalysis* 9 (7) (1997) 509–522.
- [33] V.S. Sutkar, P.R. Gogate, *Design aspects of sonochemical reactors: techniques for understanding cavitation activity distribution and effect of operating parameters*, *Chem. Eng. J.* 155 (1) (2009) 26–36.
- [34] S.J. Coleman, *Scale-up of Enface Electrochemical Reactor Systems (PhD Thesis)*, Newcastle University, 2015 pp. 76–78.
- [35] T. Kikuchi, T. Uchida, *Calorimetric method for measuring high ultrasonic power using water as a heating material*, *Journal of Physics: Conference Series*, IOP Publishing, 2011.
- [36] S.J. Coleman, *Scale-up of Enface Electrochemical Reactor Systems (PhD Thesis)*, Newcastle University, 2015 pp. 82–84.
- [37] P.R. Birkin, S. Silva-Martinez, *A study of the effect of ultrasound on mass transport to a microelectrode*, *J. Electroanal. Chem.* 416 (1–2) (1996) 127–138.
- [38] N. Ibl, K. Schadeegg, *Surface roughness effects in the electrodeposition of copper in the limiting current range*, *J. Electrochem. Soc.* 114 (1) (1967) 54–58.
- [39] S.J. Coleman, *Scale-up of Enface Electrochemical Reactor Systems (PhD Thesis)*, Newcastle University, 2015 pp. 88–89.
- [40] J.R. Selman, C.W. Tobias, *Unsteady-state effects in limiting current measurements*, *J. Electroanal. Chem. Interfacial Electrochem.* 65 (1) (1975) 67–85.
- [41] E.J. Fenech, C.W. Tobias, *Mass transfer by free convection at horizontal electrodes*, *Electrochimica acta* 2 (4) (1960) 311–325.
- [42] P.R. Gogate, et al., *Cavitation reactors: efficiency assessment using a model reaction*, *AIChE J.* 47 (11) (2001) 2526–2538.
- [43] J.C. Eklund, et al., *Voltammetry in the presence of ultrasound: a novel sono-electrode geometry*, *Electrochimica acta* 41 (9) (1996) 1541–1547.
- [44] S. Roy, P.N. Pinturo, *Analysis of mixed natural and forced convection copper deposition below the limiting current*, *Electrochimica acta* 38 (10) (1993) 1461–1470.
- [45] S.J. Coleman, *Scale-up of Enface Electrochemical Reactor Systems (PhD Thesis)*, Newcastle University, 2015 pp. 161–170.